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MECHANISM OF THE OXIDATION OF PROPENE

V. Ya. Shtern and S. S. Polyak
Inst of Chem Phys, Acad of Sci SSSR
Submitted by Acad N. N. Semenov
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[Tables referred to are appended.]

In 1949, we published [1] quantitative results of chemical research into high-temperature and low-temperature oxidation of the mixture $C_3H_6 + O_2$. On the basis of these data, we tried to add up the balance of C, H_2, and O_2 through the entire course of the reaction. As seen in Table 1, the balance adds up with sufficient accuracy. Here it is apparent that over the entire run of the reaction, the amount of water obtained (the only product not determined by analysis but by difference from the balance) is equal to the sum of CO and CO_2. In low-temperature oxidation (see Table 2) there is a disparity between the amount of carbon burned and that found in the reaction products, a disparity which increases with the extent of the transformation. This amount of carbon escaping analysis is explained as due to the polymerization of formaldehyde which takes place during low temperature oxidation. Its calculation leads to the same agreement between the quantities of water and the sum of CO and CO_2 which was noted for the high-temperature reaction.

Comparison of the results of low- and high-temperature oxidation of propene leads to the conclusion, as was shown previously [1], that there is a significant resemblance between processes in both temperature ranges. Apart from what was said in the previous report, a very important argument supporting this is the fact that at both temperature ranges, identical quantities of oxygen are consumed for the same amount of converted propene throughout the course of the reaction.

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50X1-HUM

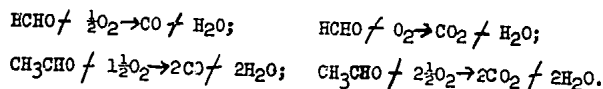Supporting points on which the scheme is based are as follows:

1. The close similarity of chemical processes established for high- and low-temperature oxidation is a reflection of the same radical-chain mechanism for both temperature ranges.

Low-temperature flashing is not reflected in this scheme, being a side process of no significance in the total reaction of oxidation.

2. Over its entire extent, the process of oxidation of propene leads to the conversion of this substance into C_2H_4, HCHO, CH_3CHO and subsequent oxidation of the aldehydes, into CO, CO_2, and H_2O.

3. HCHO formed in the reaction is not a degradation product of CH_3CHO. As was shown by special experiments, addition of CH_3CHO to the original propene-oxygen mixture does not increase the yeild of HCHO.

4. Further oxidation of the aldehydes proceeds according to the following over-all equations:

$$HCHO + \tfrac{1}{2}O_2 \to CO + H_2O; \qquad HCHO + O_2 \to CO_2 + H_2O;$$

$$CH_3CHO + 1\tfrac{1}{2}O_2 \to 2CO + 2H_2O; \qquad CH_3CHO + 2\tfrac{1}{2}O_2 \to 2CO_2 + 2H_2O.$$

5. The sum of the quantities of CO $+$ CO_2 formed is equal over the entire run of the reaction to the amount of water formed.

6. CH_3CHO brings about the degenerate-branched chacter of the oxidation.

Scheme of the Oxidation

0. $C_3H_6 + O_2 \to \dot{C}_3H_5 + HO_2$ 6. $\dot{H}CO + C_3H_6 \to HCHO + \dot{C}_3H_5$

1. $\dot{C}_3H_5 + O_2 \to C_3H_5O\dot{O}$ 7. $\dot{C}H=CH_2 + C_3H_6 \to C_2H_4 + \dot{C}_3H_5$

2. $C_3H_5O\dot{O} \to HCHO + \dot{C}H_2CHO$ 8. $CH_3CHO + O_2 \to \dot{C}H_2CHO + HO_2$

3. $\dot{C}H_2CHO + C_3H_6 \to \dot{C}_3H_5 + CH_3CHO$ 9. $2HCHO + O_2 \to$ end products

4. $C_3H_5O\dot{O} \to H_2O + CO + \dot{C}H=CH_2$ 10. $2CH_3CHO + O_2 \to$ end products

5. $\dot{C}H=CH_2 + O_2 \to HCHO + \dot{H}CO$ 11. $C_3H_5O\dot{O} \to$ breaking away

In the beginning stages of the oxidation of C_3H_6, when only traces of CO and CO_2 are detected, it may be assumed that practically the entire amount of aldehydes it covered by the analysis. In high-temperature oxidation of propene, 165 seconds after the introduction of the mixture into the reaction vessel, the following were found: HCHO, 4.03 mm; CH_3CHO, 2.3 mm; C_2H_4, 0.7 mm, and traces of CO and CO_2. In low-temperature oxidation of propene, 25 minutes after introduction of the mixture into the reaction vessel, the following were found: HCHO, 7.1 mm, CH_3CHO 3.9 mm, C_2H_4, 1.2 mm, and traces of CO and CO_2. From this, it follows that in the beginning stages of the reaction, (a) the ratio of the actually formed quantities of HCHO to CH_3CHO is close to 2; and (b) the ratio of the quantity of formed C_2H_4 to the actually formed quantity of HCHO is close to 1/5.
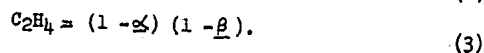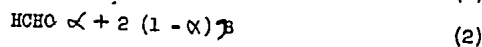
Taking the rate of the first reaction of the scheme to be 1, the rate of the second will be α, of the fourth $1 - \alpha$, of the fifth $(1 - \alpha)\beta$ and of the seventh $(1 - \alpha)(1 - \beta)$, where $\alpha < 1$ and $\beta < 1$. Using these designations, we get for the quantities of actually formed products (i.e., without considering their furthur oxidation):

- 2 -

CONFIDENTIAL

50X1-HUM

$$CH_3CHO = \alpha \qquad (1)$$

$$HCHO \quad \alpha + 2(1-\alpha)\beta \qquad (2)$$

$$C_2H_4 = (1-\alpha)(1-\beta). \qquad (3)$$

Then, for the beginning stages of the reaction,

$$\frac{HCHO}{CH_3CHO} = \frac{\alpha + 2(1-\alpha)\beta}{\alpha} = 2$$

$$\frac{C_2H_4}{HCHO} = \frac{(1-\alpha)(1-\beta)}{\alpha + 2(1-\alpha)\beta} = \frac{1}{5}$$

whence $\alpha = 0.525$ and $\beta = 0.55$.

Since α determines the relationship of two monomolecular processes with the same radical $C_3H_5O\dot{O}$ (reactions 2 and 4), it remains constant throughout the reaction.

From the scheme, we get

$$\beta = \frac{K_5(C_2H_3)(O_2)}{K_5(C_2H_3)(O_2) + K_7(C_2H_3)(C_3H_6)} = \frac{1}{1 + \frac{K_7}{K_6}\frac{(C_3H_6)}{(O_2)}} \qquad (4)$$

Thus, the value of $\underline{B}$ depends on the ratio $(C_3H_6)/(O_2)$, which changes from 1.02 to 4.57 and from 1.1 to 6.6 at the end of the reaction in the high- and low-temperature regions, respectively.

Substituting the values for $\underline{B}$, C_3H_6, and O_2 in equation 4 for the moment of the reaction which corresponds to 165 seconds for the high-temperature regions and 25 minutes for the low-temperature regions, we find the relation of k_7/k_5. From the analytical data on $(C_3H_6)/(O2)$ during the course of the process and the relation of k_7/k_5, $\underline{B}$ is determined for any moment of the reaction.

Knowing α, $\underline{B}$, and the amount of consumed propene, it is possible to determine the actual amounts of formaldehyde and acetaldehyde by using equation 1 and 2. Deducting from them the analytically determined amounts of aldehydes, we find the quantity of aldehydes subjected to oxidation, i.e., the amount of CO and CO_2 formed. Furthermore, CO, obtained by reaction 4, is determined as the sum

$$\tfrac{1}{2}[(HCHO_{initial}) - (CH_3CHO)_{initial}] + (C_2H_4).$$

Table 3 contains the results of calculations of this type for the high- and low-temperature regions. As we can see, the calculated amounts of CO correspond well to the analytically determined quantities of $CO + CO_2$, which is a confirmation of the proposed chain mechanism.

[Appended tables follow.]

Table 1. Balance in mm of C, O_2, and H_2 Along the Course of High-Temperature Oxidation of the Mixture $C_3H_6 + O_2$ (T = 370°; P initial = 220 mm, T = 2 min 35 sec).

Moment of Reaction in sec After Introduction of Mixture to Reaction Vessel	C			O_2			H_2			CO/CO_2
	Consumed	Found in Formed Substances	Remainder	Consumed	Found in Formed Substances	Remainder	Consumed	Found in Formed Substances	Remainder	
190	57	52.5	4.5	32.5	23.55	8.95	57	35.5	21.5	17.2
191.5	61.5	57.25	4.25	35	25.4	9.6	61.5	39	22.5	18.9
195	98.1	92.9	5.2	56	41.6	14.4	98.1	65.4	32.7	28.7
197.5	105	102.3	2.7	62	45.8	16.2	105	70.4	34.6	33
202	120	114	6	75	49.7	25.3	120	73.7	46.3	41
207.5	135	135.9	-	89.6	59.4	30.2	135	80.5	54.5	53.4
215	153	146.6	6.4	95.5	64.5	31	153	83.5	69.5	63.1

/* Induction period

50X1-HUM

Table 2. Balance in mm of C, O_2, and H_2 Along the Course of Low-Temperature Oxidation of the Mixture $C_3H_6 + O_2$
($T = 300°$; $P_{initial} = 320$ mm, $\tau = 30$ min 45.6 sec) (case of three cold flames)

Moment of the Reaction	C					O_2			
	Con-sumed	Found in Formed Sub-stances	Differ-ence	Spent in Polymeri-zation	Remainder After Cal-culation of Polymer-ization	Con-sumed	Found in Formed Sub-stances	Spent in Polymeri-zation	Remain-der
30 min 40.5 sec	72	67.2	4.8	3	1.8	43	30.5	1.5	11.0
End of τ (before first cold flame)	93	85.8	7.2	4.8	2.4	53	37.6	2.4	13.0
End of first cold flame	105	97.1	7.9	5.2	2.7	62.5	44	2.6	15.9
Before second cold flame	111	100	11	8.2	2.8	68.5	45	4.1	19.4
End of second cold flame	126	109.7	16.3	12.8	3.5	78	49.3	6.4	22.3
Before third cold flame	144	118.7	25.3	21.5	3.8	91.5	54.75	10.75	26
End of third cold flame	171	131.5	39.5	35	4.5	110.5	60.75	17.5	32.25
End of reaction	213	168.6	44.4	39	5.4	144	82.13	19.5	42.37

H_2

Consumed	Found in Formed Substances	Spent in Polymerization	Remainder	$CO + CO_2$
72	46.05	3	23	21.9
93	61.4	4.8	26.8	25.4
105	64.5	5.2	35.3	33.7
111	62.8	8.2	40	38.3
126	65.7	12.8	47.5	44.8
144	69.1	21.5	53.4	50.7
171	67.5	35	68.5	63
213	75.5	39	98.5	93.4

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- 6 -

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50X1-HUM

50X1-HUM

Table 3. Comparison of Quantities of $(CO + CO_2)$ Calculated According to the Scheme With Quantities Found Analytically in the Course of Oxidation of the Mixture $C_3H_6 + O_2$

(quantities of substances in mm)

Moment of the Reaction	B*	$\frac{C_3H_6}{O_2}$	C_3H_6 Initial	Analytically Found			Actually Formed		HCHO, Lost in Poly-merization	$CO + CO_2$	
				CH_3CHO	HCHO	C_2H_4	CH_3CHO	HCHO		Calculated From Scheme	Analyti-cally Found
High-Temperature Region ($T = 370°$; $P_{initial} = 220$ mm; $\alpha = 0.525$)											
165 sec	0.55	1.02	3.5	2.3	4.03	0.7	--	--	--	--	--
190 "	0.515	1.18	19.0	7.1	12	3.0	10.0	20.1	--	21.9	17.2
191.5 "	0.511	1.2	20.5	7.1	14.85	3.5	10.75	21.6	--	21.2	18.9
195 "	0.463	1.45	32.7	12.3	25.6	4.8	17.2	33.5	--	30.6	28.7
197.5 "	0.422	1.59	35	12.5	27.2	6	18.4	35.7	--	35	33
202 "	0.378	2.06	40	12.3	28	8	21.0	40.2	--	47.2	41
207.5 "	0.268	3.46	45	13	28.5	10	23.6	44.35	--	57.3	53.4
215 "	0.214	4.57	51	13.5	28.8	10.7	26.7	46.4	--	68.1	63.1
Cold-Flame Region ($T = 300°$; $P_{initial} = 320$ mm; $\alpha = 0.525$)											
30 min 16.5 sec	0.545	1.1	19	6.0	14.1	2.5	9.95	19.6	--	--	--
30 min 16.5 sec	0.53	1.16	24	9	19	3.75	12.6	24.7	3.0	19.8	21.9
End of τ**	0.52	1.21	31	12	25	4.8	16.2	32.0	4.8	23.3	25.4
End of first cold flame	0.505	1.29	35	12.3	26	5.3	18.3	36.0	5.2	30.9	33.7

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Before second cold flame	0.49	1.35	37	10.5	24	7.2	19.4	38	8.2	40.1	38.3
End of second cold flame	0.475	1.46	42	11.1	24.6	7.9	22	42.9	12.8	45.6	44.8
Before third cold flame	0.44	1.67	48.	11.6	25.5	8.3	25.5	48.6	21.5	48.8	50.7
End of third cold flame	0.38	2.15	57	11.0	24.0	9.0	30	56.9	35	60.5	63
End of reaction	0.167	6.6	71	12.3	27.4	9.8	37.2	67.8	39	76.3	93.4

*For calculating the actual quantities of HCHO, we made use of the average value of $\underline{P}$ for every moment of the reaction

**End of induction period, i.e., moment of origination of first cold flame

Bibliography

1. V. Ya. Shtern and S. S. Polyak, DAN SSSR, Vol LXV, No 3, 311 (1949)

2. V. Ya. Shtern and S. S. Polyak, DAN SSSR, Vol LXVI, No 2, 235 (1949)

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- 8 -

CONFIDENTIAL

50X1-HUM